

1,164,424

# PATENT SPECIFICATION

NO DRAWINGS

1,164,424



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## COMPLETE SPECIFICATION

### Improvements relating to the Dyeing and Finishing of Cellulose Ester Fibre Material from a Single Bath

We, J. R. GEIGY A.G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention concerns a process for the dyeing and finishing of cellulose ester fibre material from a single bath, the treatment liquor used for this purpose as well as the cellulose ester fibre material dyed and finished by this process.

10 It is known that cellulose ester fabric can be dyed with dispersion dyestuffs from an aqueous liquor and that the dyed fabric can then be given a finish suitable for the intended purpose, also from an aqueous liquor. The treatment in water, however, has various drawbacks. For example, the structure of the goods is disadvantageously affected and fabric having an undesirable, floppy feel (or 'handle') is obtained. The extensive deterioration of the feel cannot be completely corrected later, even by the use of feel improvers. It has already been suggested, therefore, that dyeing be performed from organic solvents and after thermofixing the dyestuffs, that the finishing agent be applied from organic solvents onto the fabric in a second bath. This two-bath treatment however, still suffers from various drawbacks. For example, in order to attain dyeings which are fast to wet treatments and crocking, the addition of auxiliaries is required in such amounts that they often have a disadvantageous effect

15 on the desired finish. Also, the subsequent application of finishing agents onto the fabric dyed from an organic bath can sometimes, depending on the agent used, cause an alteration in the shade which makes the reproduction of dyeings to sample considerably more difficult and/or such subsequent application of finishing agents can affect detrimentally the fastness to light of the dyeing. In addition, the structure of

20 the fibre can be damaged by the two heat treatments involved.

25 It has now been found that the drawbacks mentioned can be avoided when cellulose ester fibre material is simultaneously dyed and finished from a single bath. Therefore, the present invention provides a process for the dyeing and finishing of cellulose ester fibre material from a single bath by impregnating or printing this material with a solution containing, in combination, organic dyestuff and finishing agent and, optionally, dyeing auxiliaries in a mixture of solvents consisting essentially of

30 a) at least 50% by weight of optionally halogenated hydrocarbon boiling between 35 70 and 150°C, and  
b) at most 50% by weight of water miscible organic solvent boiling below 210°C, and in the case of the dye solution being applied by impregnating, then removing a large amount of excess treatment liquor from the fibre material, and fixing the dyeing or print by means of thermofixing at temperatures below the softening point of the fibre material.

35 The said impregnation of the fibre material may be performed by known techniques, e.g. padding or printing.

40 The dyeings obtained by the process according to the invention on cellulose ester fibres possess unexpectedly good fastness to wet treatments such as washing,

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alkaline milling, perspiration, sea water, and good fastness to crocking and to dry cleaning, often without requiring any addition of auxiliaries enhancing these fastness properties, or much small amounts of such auxiliaries than would be required in the known two-bath treatments.

5 No explanation can at present be given for this unexpected result of using the single-bath process according to the invention. 5

10 Suitable hydrocarbons boiling between 70 and 150°C which can be used as component a) of mixtures of solvents usable according to the invention are, e.g. aromatic hydrocarbons such as toluene or xylene; mainly the mixtures of solvents as defined contain at least 50% by weight of halogenated, particularly chlorinated, hydrocarbons such as chlorobenzene, and preferably, aliphatic halogenated hydrocarbons having at most two carbon atoms such as chlorinated hydrocarbons, e.g. carbon tetrachloride, tetrachloroethane or dibromoethylene, tri- or tetra-chloroethylene being preferred. Also mixtures of such solvents can be used as component a) of the treatment liquor. 15

15 Water miscible organic solvents boiling below 210°C which can be used as component b) of the mixture of solvents usable in the process according to the invention are, e.g. monovalent aliphatic alcohols such as *n*- or iso - propanol; alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl or monoethyl ether; then also furfuryl or tetrahydrofurfuryl alcohol; or divalent aliphatic alcohols such as ethylene glycol or 1,2-propylene glycol; also aliphatic ketones having at most five carbon atoms such as acetone; cyclic ethers such as dioxan or tetrahydrofuran; amides of fatty acids having at most five carbon atoms such as dimethyl formamide or dimethyl acetamide; amides of carbonic acid such as tetramethyl urea, or tertiary organic amines such as pyridine; also mixtures of such solvents can be used as component b) of the treatment liquor. The amides of fatty acids, especially dimethyl acetamide, are preferred as component b) of the mixture of solvents. 20 25

20 The composition of the mixture of solvents depends on the solubility of the dyestuffs and finishing agents to be used. It should be such that there is a homogeneous, clear or opalescent solution. Preferably, mixtures of solvents are used which consist of 85 to 99.5% by weight of a halogenated hydrocarbon boiling between 70 and 150°C and 15 to 0.5% by weight of an amide of a fatty acid having at most five carbon atoms. 30

25 30 Organic dyestuffs which can be used according to the invention are water soluble dyestuffs and color or dye salts, particularly however, dispersion dyestuffs. They can belong to any class of dyestuffs desired. For example, they can be metal-free or heavy metal-containing azo dyestuffs, which comprises also the formazane dyestuffs, as well as anthraquinone, nitro, methine, especially styryl, azostyryl, naphthoperinone, quinophthalone, oxazine, 5-amino-8-hydroxy-1,4-naphthoquinone or phthalocyanine dyestuffs. 35 40

35 40 The so-called acid wool dyestuffs of the azo and anthraquinone series which contain a sulphonate or carboxylic acid group are particularly suitable as water-soluble dyestuffs for use in the process according to the invention. As azo dyestuffs, acid, metal-free and heavy metal-containing mono- or dis-azo dyestuffs can be used; as heavy metal-containing azo dyestuffs, particularly chromium- or cobalt-containing monoazo dyestuffs containing no acid and basic water-solubilising groups, which dyestuffs contain 2 molecules of azo dyestuff bound to one metal atom, can be used. As anthraquinone dyestuffs, especially 1-amino-4-aminolamino-anthraquinone-2-sulphonic acids are to be mentioned. 45

45 50 As dispersion dyestuffs, metal-free azo, styryl, naphthoperinone, quinophthalone, nitro and anthraquinone dyestuffs containing no acid, salt-forming groups are preferred.

50 55 Salts having a coloured organic cation and uncoloured organic anion, salts having a colourless organic cation and coloured organic anion, and salts having a coloured organic cation and coloured organic anion are used as soluble dye salts. The coloured part of these dye salts can be taken from any one of the classes of dyestuffs mentioned above. Preferred coloured cations, for example, belong to the di- and tri-phenylmethane, rhodamine, oxazine and thiazine series; these can also be azo dyestuffs containing quaternary ammonium groups, particularly cyclammonium groups. The coloured anions of such dye salts are, e.g. the ions of dyestuff carboxylic acids or, more advantageously, of dyestuff sulphonic acids or of metal complex dyestuffs which consist of one equivalent of trivalent, co-ordinatively hexavalent heavy metal such as chromium or cobalt and of two equivalent of bicyclic metal complex-forming dyestuffs, e.g. from the class of *o,o'*-dihydroxy or *o*-hydroxy-*o'*-carboxyazo or -azomethine dyestuffs. For example, precipitation products of di- or tri-phenylmethane or rhod-

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amine dyestuffs with optionally sulphated chromium or cobalt complexes of *o,o'*-di-hydroxy- or *o*-hydroxy-*o'*-carboxy-azo dyestuffs can be used as such dye salts. As colourless cations in these salts those of primary, secondary or tertiary organic amines of the aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic series or of cyclic amines can be used. In salts having coloured cations, principally the radicals of organic acids, particularly aromatic sulphonic acid, e.g. anions of alkyl - alkoxy - benzene sulphonate acids are mentioned as colourless anions. 5

The treatment liquor to be used contains, e.g. 0.1 to 10% by weight of one or more of the dyestuffs mentioned, depending on the desired depth of shade. 10

Finishing agents which can be used according to the invention are, e.g. those which have an oil and water repellent action, have a desirable effect on the handle of the fibre materials treated, provide anti-slipping or antistatic properties, bring about inflammability, have a bacteriostatic effect or prevent attack by microorganisms, e.g. by fungi. By making a suitable choice, several of these finishing effects can also be attained simultaneously with one finishing agent, for example, a repellent action simultaneously to oil and water, or water repellency combined with a full, soft feel. 15

On the other hand, however, several finishing agents can be combined with each other in order to attain the desired effects in each case. 20

The prerequisite for the use of the finishing agents is that they, or optionally mixtures thereof, are soluble in the mixture of solvents used according to the invention. It is advantageous if the finishing agents are added in liquid form to the treatment liquor, i.e. dissolved in any organic solvent or solvent mixture desired. 25

Such finishing agents suitable for the aforesaid single-bath dyeing and finishing process are, for example, the following: 25

a) A condensation product of formaldehyde and either urea or melamine in a molar ratio of from 1.5 to 4.5 of the former reactant per amino group in the urea or melamine, at least one of the resulting methylolamino groups in the condensation product being esterified by (i) an aliphatic carboxyl radical of from 8 to 22 carbon atoms, or being etherified with (ii) an aliphatic hydrocarbon radical of from 8 to 22 carbon atoms, or with (iii) a radical of the formula R—CO—NH—CH<sub>2</sub>—, wherein R represents an aliphatic hydrocarbon radical of from 7 to 21 carbon atoms, at least part of the balance of methylol groups being etherified with an alkyl having at most two carbon atoms. 30

The method of preparing such condensation products is described in British patent No. 726,661, published March 23, 1955; in German application laid open to public inspection No. 1,233,874, published February 9, 1967; and in German application laid open to public inspection No. 1,044,402, published November 20, 1958. 35

These condensation products impart to the fibre material treated therewith a limited hydrophobic effect and a pleasant handle, which may be varied by the additional use of fatty compounds such as paraffin, fat, e.g. glycerol higher fatty acid esters or waxes, e.g. myristyl or cetyl higher fatty esters. 40

b) A condensation product as defined under a) and etherified with (ii), and being simultaneously condensed with 0.5 to 10 mols of a free aliphatic or aromatic dicarboxylic acid having from 4 to 12 carbon atoms, especially maleic or phthalic acid, or the anhydride of such an acid. A method of producing these condensation products is described in Swiss patent No. 388,901, published June 30, 1965. 45

Into this final product may be condensed further 0.2 to 0.6 mol of an aliphatic monocarboxylic acid having 8 to 22 carbon atoms per mole of melamine, as described in Example 2 of said Swiss patent. 50

These condensation products impart to the fibre material treated therewith good water-repellency and a pleasant handle which may be varied with the above mentioned fatty compounds. 55

By applying condensation products as defined under (a) or (b), without or with a fatty compound jointly, with an alcoholate of an alkanol or alkanediol having each at most five carbon atoms and a trivalent or tetravalent metal of columns III or IV of the Periodic system of Mendelejev, especially aluminium, titanium or zirconium, to the fibre material the water repellent effect is further improved. 60

The preparation of such alcoholates is described for example in the German patent application C 1891 IVd/12 o, published August 16, 1951; German applications laid open to public inspection No. 1,116,412, published November 2, 1961; No. 1,114,176, published September 28, 1961, and No. 1,076,110, published February 25, 1960. 60

c) Organopolysiloxanes used as textile finishing agents in the process according to the invention, which impart to cellulose ester fibres treated therewith a soft handle and a limited hydrophobic effect; such polysiloxanes are especially methyl hydrogen polysiloxanes, dimethylpolysiloxanes or mixtures of both types of polysiloxanes.

5 Such organo polysiloxanes are prepared by known methods, e.g. as described in German patent No. 925,225, published August 5, 1954 or in German patent No. 864,152, published March 20, 1952.

10 The water-repellency imparted to the fibre material by using said organopolysiloxanes may be essentially improved by jointly applying known hardening catalysts, e.g.

15 (a) an alcoholate of a lower alkanol or a lower alkandiol and a trivalent or tetravalent metal of columns III or IV of the Periodic system of Mendelejev, especially aluminium, titanium or zirconium, the preparation of which is specified above;

15 (b) an alcoholate as said in (a) in which at least one alkoxy group has been replaced by an acyloxy group of a fatty acid of from 6 to 22 carbon atoms.

20 The production of such type of hardening catalysts is described for example in German patent application F 10 490 IVc/8k, published February 23, 1956; German patent application laid open to public inspection No. 1,123,308, published February 8, 1962; German patent No. 1,041,942, published October 30, 1958; or German patent No. 880,292, published October 16, 1952.

25 (c) a condensation product of (i) alcoholates of tri- or tetravalent metals, especially aluminium, zirconium, or titanium, and alkanols, or alkandiols of from 2 to 6 carbon atoms, or mono-alkyl ethers having at most two carbon atoms of the aforesaid alkandiols, and (ii) formaldehyde in a molar ratio of (i):(ii), in the range of from 1:1 to 1:10.

30 These condensation products may be stabilised against precipitations caused by moisture by the addition of a metal soap of a fatty acid of at least 5, and preferably 6 to 18 carbon atoms and a 2-, 3- or 4-valent metal, such as magnesium, calcium, strontium, barium, zinc, aluminium, titanium, tin, lead or manganese, in particular aluminium octoate, barium octoate, magnesium octoate, lead octoate, tin octoate, zinc octoate, barium oleate, calcium oleate, manganese oleate, calcium laurate, zinc laurate, aluminium stearate, magnesium stearate, zinc stearate, titanium stearate and strontium stearate in an amount of from 0.06 to 1 mol of said metal soap to 1 mol of the aforesaid condensation product.

35 The preparation of such condensation products is described in German patent applications C 41 896 IVc/8k, filed on March 29, 1967 and C 42 529 IVa/12g, filed on June 6, 1967.

40 (d) Organo-tin-compounds such as diorganotin-diacylate as described in German patent application laid open to public inspection No. 1,225,640, published September 29, 1966.

40 (e) Salts of zinc with an organic fatty acid, containing from 6 to 12 carbon atoms.

45 (d) Fatty compounds such as paraffins, oils, waxes, fats or esters of higher fatty acids with alcohols having at most five carbon atoms, and their mixtures. They are suitable for improving the handle of the fibre materials.

50 (e) The condensation products of alcoholates as defined above under (c) with formaldehyde, without and with stabilising by addition or co-condensation of metal soaps as above mentioned under c,  $\gamma$ . They are per se suitable as antislipping agents. The handle of the fibre material may be varied by jointly applying fatty compounds as defined under (d).

55 (f) Polymerisates or mixtures of polymerisates such as those of ethylene and propylene (as described in German patent application laid open to public inspection No. 1,090,628, published October 13, 1960), of acrylate ester or methacrylate ester or esters of vinyl alcohol with fatty acids having at most five carbon atoms (as described in German patent No. 626,920, published March 5, 1936), or their copolymerisates with acrylonitrile (as described in German patent No. 653,084, published November 13, 1937), methacrylate esters of higher alcohols (as described in German application No. 1,002,281, published February 14, 1957), styrene or its derivatives (as described in German patent No. 534,636, published September 23, 1931 and German applica-

tion No. 1,088,019, published September 1, 1960), copolymerisates of styrene and styrene derivatives with e.g. butadiene, copolymerisates of mono-esters of  $\alpha,\beta$ -ethylenedicarboxylic acids with copolymerisable monomers (as described in German patent No. 1,077,631, published March 17, 1960), terpene (as described in French patent No. 1,185,745, délivré-date February 16, 1959), and other polymerisates and copolymerisates, e.g. of vinyl chloride and vinyl isobutyl ether, as far as they are soluble in organic solvents. These polymerisates are used to impart to the fibre material a fuller handle. 5 5

g) Organic compounds containing a perfluoro carbon "tail" of from 4 to 12 fully fluorinated carbon atoms, such as copolymerisates of acrylate and methacrylate esters of perfluoro-alkane sulphonamido alkanols with other copolymerisable monomers as described in U.S. patent No. 2,803,615, published August 20, 1957. The copolymerisates obtained are coagulated, dried and dissolved in a mixture of carboxylic esters, e.g. butylacetate and halogenated hydrocarbons. These compounds are suitable to impart to the fibre material oil- and water-repelling properties. 10 10

Other suitable finishing agents to impart oil- and water-repellency are adducts of perfluoroalkane sulphonamido alkanols having in the molecule a perfluorocarbon "tail" of from 4 to 12 fully fluorinated carbon atoms to mono-, di- or poly-isocyanates of the aliphatic, aromatic or araliphatic series. The water-repellency so obtained may be improved by reacting said fluoro compounds and di- or poly-isocyanates with an aliphatic higher alcohol. This type of fluorine compounds is described in British patent No. 999,795, published July 28, 1965 and Austrian patent No. 254,128, published May 10, 1967. Further, polymerisates of acrylate or methacrylate esters with fluorinated alkanols having at most five carbon atoms, such as hexafluoro-isopropanol, are suitable as such finishing agents. 15 15 20 25

h) Higher fatty acid esters of pentachlorophenol, which impart to the fibre material treated therewith fungistatic properties.

i) Neutralised or acidified condensation products of polyglycidylethers with polyamines. The preparation of these products, which impart to the fibre material anti-static properties, is described in Swiss application No. 3702/65, published July 14, 1967. These condensation products are brought to a high solid content and mixed with an appropriate emulsifying agent, e.g. an organic amine salt of an organic sulphonic acid. 30 30

j) Organic compounds containing phosphorous, e.g. polymerised allyl-bis-(dibromo-propyl)-phosphate or diallyl-dibromo-propyl-phosphate, copolymerisates of these compounds, or their mixtures. Such finishing agents are suitable to impart to the fibre material flameproofing properties. 35 35

k) 1,3-Diphenyl urea derivatives as described in U.S. patent No. 2,745,874, issued May 15, 1956; used as finishing agents in the process according to the invention they impart to the fibre material bacteriostatic properties. 40 40

Depending on the desired effect, treatment liquors according to the invention contain, e.g. 0.1 to 10% by weight of one or several of the finishing agents. 45 45

If necessary, the treatment liquor can also contain thickeners, advantageously, those which are soluble in the mixture of solvents defined, e.g. thickeners based on cellulose esters or polyvinyl esters, and/or small amounts of auxiliaries such as surfactants which guarantee perfect fastness to crocking of the dyeings or prints. In particular, non-ionic tensides, especially ethers and esters of polyethylene glycol consisting of a higher aliphatic hydrocarbon radical or the acyl radical of a higher fatty acid with a carbon chain of from 8 to 20 carbon atoms or an alkyl substituted phenyl radical, the alkyl chain of which having from 6 to 12 carbon atoms, and a polyether chain made up of about 2 to 20 ethyleneoxy groups have proved effective. These are preferably condensation products of one mol of a higher fatty alcohol or of a higher fatty acid of from 10 to 18 carbon atoms with 4 to 10 mols of ethylene oxide such as penta-, hepta-, or deca-ethylene glycol monolauryl or monostearyl or monooleyl ether, or the monoester of stearic or oleic acid with penta-, hepta- or deca-ethylene glycol. Also other polyglycol ethers having emulsifying properties such as higher alkylphenol polyglycol ethers, e.g. penta-ethylene glycol monononylphenol ether or tri-(1,2-propylene glycol)-monononylphenol ether, or polyglycol ethers containing 50 50 55 55

basic nitrogen, e.g. also polyglycol ethers of aliphatic, higher alkylated or higher acylated di- and poly-amines, are suitable as tensides. As such, also amides of aliphatic monocarboxylic acids containing at least one lipophilic radical with primary or secondary amines containing at least one hydroxyalkyl group having at most three carbon atoms, particularly coconut fatty acid mono- or di-hydroxy-ethylamides, optionally in admixture with the polyglycol ethers mentioned, can be used.

Polyethylene glycol mono-oleyl ethers having 4 to 10 ethyleneoxy groups are preferred.

If the use of such auxiliaries is necessary, which depends on the type of finishing agent, in general amounts up to 0.5% by weight, calculated on the total weight of the treatment liquor, are sufficient.

A preferred performance of the process according to the invention comprises

(a) impregnating said fibre material with a substantially non-aqueous clear or opalescent solution of

(a) organic dyestuff of which at least 0.5 g are soluble in every kg of said fibre material, in an amount sufficient to colour said fibre material in a desired depth,

(b) textile finishing agent in a sufficient amount to impart to said fibre material a desired degree of finish in

(c) a solvent mixture consisting essentially of

(i) 50—99.5 percent by weight of unhalogenated or halogenated hydrocarbon having a boiling point between 70 and 150°C, and

(ii) 50—0.5 percent by weight of water-miscible organic solvent having a boiling point above 100°C and below 210°C,

(d) 0—1 percent by weight of water,

(e) 0—0.5 percent by weight of further auxiliaries,

(b) mechanically removing any excess solution, and

(c) thermofixing dyestuff on, or in the impregnated fibre material at a temperature below the softening point of the latter material,

both said organic dyestuff and said textile finishing agent being compatible with each other and being soluble at least colloidally in said solvent mixture.

As fibre material which can be dyed or printed and finished in a single bath according to the invention, that made of cellulose esters, preferably cellulose-tri- and particularly -2<sub>1</sub>-acetate is meant. The fibre material mentioned can be dyed and finished in any form desired such as in the form of flakes, slubbing, yarn or — preferably — fabrics, as well as also in the form of mixed fabrics.

Cellulose ester fibre material is impregnated, e.g. by printing or spraying, preferably however, by pad dyeing. In the latter case, the fibre material is advantageously continuously passed through the treatment liquor at room temperature and then squeezed out to the desired content of treatment liquor which is 30 to 150% by weight (calculated on the weight of the goods). The main part of the mixture of solvents remaining in the fibre material is then advantageously removed by mild drying at 40—100°C, advantageously in a stream of warm dry air. After this drying process, the finishing agents can already be fully fixed and the dyestuff not fixed. This condition can easily be recognised by the insufficient fastness to dry cleaning or rubbing of the apparent dyeing.

The dyestuff is fixed onto the fibre material from which excess treatment liquor has already been removed and, if desired, which has already been dried, by thermofixing at temperatures of at least 170°C, preferably 185—210°C, but below the softening point of the fibre material. Heated air, contact heat, a treatment with high frequency alternating currents or IR irradiation are suitable for the thermofixing.

The time spent by the fibre material to be dyed in the treatment liquor, the type of drying of the impregnated material, and the duration and temperature of the thermofixing depend on the composition of the treatment liquor, particularly on the mixture of solvents. All the measures and conditions should be so adjusted to each other that sufficient swelling of the fibre for the dyestuff take-up together with maintenance of the structure of the fibre is achieved. The most favourable conditions for a given apparatus can easily be determined by a trial run.

When using a preferred treatment liquor which contains as mixture of solvents, e.g. 85 to 95% by weight of trichloroethylene and 15 to 5% by weight of methanol, or 95 to 99.5% by weight of tetrachloroethylene and 5 to 0.5% by weight of dimethyl acetamide, the time spent by cellulose ester fibre material in the treatment liquor is

between 0.1 to 20 seconds and, preferably, 0.1 to 2 seconds; the duration e.g. of the dry heat treatment in a stream of air of 170°—220°C is advantageously 10 to 120 seconds.

5 Mixtures of solvents which enable sensitive cellulose 2½-acetate and cellulose triacetate to be dyed and finished without injuring the fibre and produce an evenly good fastness to rubbing while maintaining the pliable and voluminous feel, consist of a mixture of 95—99.5% by weight of a chlorinated aliphatic hydrocarbon as hereinbefore defined such as tetrachloroethylene or trichloroethylene and 5 to 0.5% by weight of an amide, monoalkylamide or dialkylamide of a fatty acid as hereinbefore defined, particularly e.g. dimethylacetamide, which mixture can contain up to 0.5% by weight of one of the surfactants mentioned.

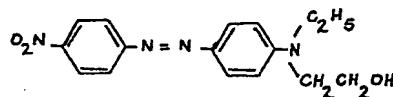
10 The process according to the invention enables cellulose ester fibre materials, particularly those made from cellulose 2½-acetate, to be dyed in pale to very deep shades and, simultaneously, finished. Because of the single bath process in mixtures of 15 organic solvents, the original voluminous, full feel of the textile material is maintained. Although according to the process of the invention, to some extent the same solvents are used as are used for the dry cleaning of these textiles, in spite of this, such dyeings have good fastness to dry cleaning. The other fastness properties however, such as fastness to wet, light and rubbing, are also good. The dyeings are distinguished 20 by excellent evenness at great colour strength, which is surprising, as after the drying process, the greater part of the finishing agents are fully fixed. In addition, in the single-bath process, it is generally unnecessary to add an auxiliary to produce optimal rubbing fastness properties and it is possible to reproduce a given shade exactly to 25 sample. The shades obtained are identical for all practical purposes to those obtained without finishing effect.

25 Compared with processes used hitherto, the single-bath process according to the invention is more economical. Finally, it is important that the solvents used can be almost completely regained and recycled into the dyeing process; thus, in contrast to previously known processes, the problem of effluent purification does not arise. 30 Also, rinsing baths are not necessary.

30 The following Examples illustrate the invention. The temperatures are given therein in degrees Centigrade.

#### EXAMPLE 1

5 g of the dyestuff of the formula



40 are dissolved in about 800 g of a mixture of solvents consisting of 767 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 19 g of a paraffin-free condensation product of melamine, paraformaldehyde, phthalic acid anhydride, 45 stearic acid and, instead of the octanol, the double quantity of octadecyl alcohol (obtained by the method described in Swiss Patent No. 388,901, Example 2) in about 100 g of tetrachloroethylene is added to make up the weight of the liquor thus obtained to 1000 g. Cellulose-2½-acetate fabric is impregnated with the clarified dye solution at room temperature, the goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot 50 airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

50 A strongly coloured, level and well developed red dyeing having good fastness to dry cleaning and perspiration is obtained. The fabric has a soft, pliable feel and a limited hydrophobic effect. The fabric simultaneously has good fungicidal properties on adding 20 g of lauric acid pentachlorophenol ester to the liquor.

55 If in this Example, instead of 30 g of dimethyl acetamide, one of the water miscible solvents mentioned in the following Table 1 column 2 is used in the amount given in column 3 with otherwise the procedure given in this Example, then level and well developed scarlet dyeings on cellulose-2½-acetate fabric which have similar good fastness properties and finishing effects are also obtained.

TABLE I

Example No.	Water miscible solvents	Amount (in g)
2	isopropanol	100
3	benzyl alcohol	100
4	<i>n</i> -butanol	80
5	ethylene glycol monomethyl ether	90
6	tetrahydrofurfuryl alcohol	90
7	ethylene glycol	50
8	1,2-propylene glycol	60
9	dioxan	100
10	diethyl formamide	100
11	dimethyl formamide	30
12	pyridine	50

If in Examples 1 to 12, the same amount of one of the hydrocarbons or chlorinated hydrocarbons given in the following Table II column 2 are used instead of tetrachloroethylene and otherwise the procedure described in Example 1 is followed, then level and well developed red dyeings on cellulose-2½-acetate fabric having a corresponding feel are also obtained.

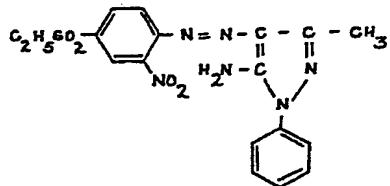
TABLE II

Example No.	Hydrocarbon or chlorinated hydrocarbon
13	toluene
14	xylene
15	trichloroethylene
16	carbon tetrachloride

If in Examples 1 to 16, cellulose triacetate is used instead of cellulose-2½-acetate then with otherwise the procedure given well developed and strongly coloured red dyeings on the fibre material mentioned are obtained which have corresponding finishing effects.

### EXAMPLE 17

5 g of the dyestuff of the formula

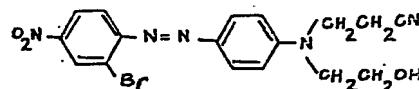


5 are dissolved in about 800 g of a mixture of solvents consisting of 767 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 9 g of a paraffin-free condensation product of melamine, paraformaldehyde, phthalic acid anhydride, 10 stearic acid and, instead of the octanol, the double quantity of octadecyl alcohol (obtained by the method described in Swiss Patent No. 388,901, Example 2) in about 100 g of tetrachloroethylene is added to make up the weight of the liquor thus obtained to 1000 g. Cellulose-2½-acetate fabric is impregnated with the clarified dye solution at room temperature, the goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

15 A level and well developed yellow dyeing of strong colour depth having good fastness to dry cleaning (which is, when evaluated by the SNV—Test No. 92825/1957, at least about 20% better than that obtained with a two-bath process), and to perspiration is obtained. The fabric has a soft, pliable feel and a limited hydrophobic effect. The fabric simultaneously has good fungicidal properties on adding 20 g of lauric acid pentachlorophenol ester to the liquor.

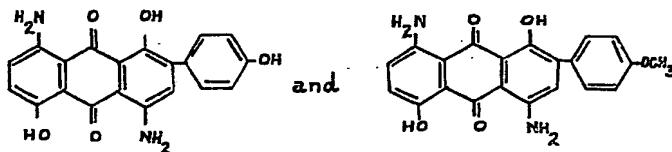
20 When the above-obtained finished dyeings are compared with finished dyeings on cellulose-2½-acetate fabric first dyed with the above dyestuff and then finished in a subsequent organic solvent bath with the above finishing agent, then the hydrophobic value of the dyeings obtained by the single-bath procedure of the above Example, when subjected to the AATCC Test No. 22—1952, is about 40% better than that of the dyeings obtained in the two-bath method.

25 **EXAMPLE 18**  
Example 17 is repeated, but with 3 g of the dyestuff of the formula



30 in lieu of 5 g of the dyestuff of Example 17, and red dyeings on cellulose-2½-acetate fibres are obtained which have better fastness to dry cleaning, transpiration, washing with soap and water of 40°, and especially an about 100% better light fastness than dyeings obtained with the same dyestuff and finishing agent applied from separate organic solutions applied successively.

35 **EXAMPLE 19**  
Example 17 is repeated but with 2 g of a mixture of the dyestuffs of the formulae



40 in a weight ratio of about 1:1, whereby blue dyeings on cellulose-2½-acetate fibres are obtained which have better fastness to transpiration, show better hydrophobic effect, and, especially a 50% better fastness to washing (evaluated according to the SNV—Test No. 95811/1961) than dyeings obtained in a two-stage dyeing and finishing treatment.

45 By repeating Examples 1 to 19, but using instead of the dyestuffs mentioned therein each of those listed in column 2 of the following Table III, and following the procedure given in the Example, level and well developed, strongly coloured cellulose-2½-acetate dyeings are also obtained having the shades given in column 3 of the Table, and similar good fastness properties. The fabrics have a pleasant, smooth handle.

TABLE III

Example No.	dyestuff	shade on cellulose- 2 $\frac{1}{2}$ -acetate
20		greenish yellow
21		yellowish orange
22		orange
23		scarlet
24		ruby
25		reddish yellow
26		yellow
27		greenish yellow

TABLE III (Continued)

**EXAMPLE 31**

5 g of the same yellow dyestuff as used in Example 17 are dissolved in about 800 g of a mixture of solvents consisting of 767 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mole ratio about 1:7.5) and 150 g of a solution are added, consisting of 100 g tetrachloroethylene and 50 g of a mixture of ( $\alpha$ ) a condensation product as used in Example 17, ( $\beta$ ) paraffin wax, and ( $\gamma$ ) tetra-n-propyltitanate, containing 16.5% Ti, in a weight ratio of ( $\alpha$ ):( $\beta$ ):( $\gamma$ ) of 1:2:1.5.

10 in a weight ratio of ( $\alpha$ ):( $\beta$ ):( $\gamma$ ) of 1:2:1.5.

Cellulose-2 $\frac{1}{2}$ -acetate fabric is impregnated with the clarified, intensively yellow coloured dye solution at room temperature, excess treatment liquor is squeezed out to 100% of the dry weight of the goods and the impregnated fabric is dried in a 40—80° hot air stream. The dyeing is then thermofixed for 60 seconds by IR irradiation at 180—210°C.

15 A level and well developed yellow dyeing is obtained which has good fastness to dry cleaning and perspiration. The fabric has very good water-repellent properties and has a pleasant, smooth handle.

Similar good results are obtained by replacing the tetra-*n*-propyltitanate used in the above Example 31 by an equivalent amount of zirconium butylate and otherwise following the procedure described in the Example.

If the procedure described in the Example is followed but the dyeing and finishing are not performed simultaneously but separately in two different baths, then the dyeings are not fast, particularly not fast to rubbing and dry cleaning. In order to attain dyeings having good wet and rubbing fastness properties, an auxiliary, e.g. condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5), must be added to the first bath. This auxiliary, however, gives wetting properties to the fabric which cannot be completely compensated by a corresponding finishing of the dyed material in a second bath so that dyeings having a considerably worse water repellent effect are obtained.

## EXAMPLE 32

By using in lieu of the dyestuff employed in Example 31 3 g of the red dyestuff used in Example 18, and otherwise following the procedure of Example 31, there is obtained a red dyeing of very good water-repellent properties and pleasant, smooth handle.

## EXAMPLE 33

By using in lieu of the dyestuff employed in Example 31 3 g of the dyestuff mixture used in Example 19, and otherwise following the procedure of Example 31, there is obtained a blue dyeing of very good water-repellent properties and pleasant, smooth handle.

## EXAMPLE 34

5 g of the same yellow dyestuff as used in Example 17 are dissolved in 800 g of a solvent mixture consisting of 767 g of tetrachloroethylene and 30 g of dimethyl acetamide, and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio of about 1:7.5), and 150 g of a solution consisting of 100 g of tetrachloroethylene and 50 g of a mixture of (α) a condensation product as used in Example 17, (β) paraffin wax, and (γ) tetra-n-propyltitanate, containing about 16.5% Ti, in a weight ratio of (α):(β):(γ) of 1:2:1.5, and 50 g of a 30% solution of a vinyl chloride/vinyl isobutyl ether copolymerize dissolved in a mixed solvent consisting of 1 part by volume of butyl acetate and 1 parts by volume of 1,1,1-trichloroethane are added thereto.

Cellulose-2½-acetate fabric is impregnated with the clarified, intensively yellow coloured dye solution at room temperature, excess treatment liquor is squeezed out to 100% of the dry weight of the goods and the impregnated fabric is dried in a 40—80° hot air stream. The dyeing is then thermofixed for 60 seconds by IR irradiation at 180—210°.

The dyed fabric thus obtained has a 30% better fastness to crocking (SNV—Test No. 95831/1957), a 30% better fastness to perspiration (SNV—Test No. 95824/1961) and a 40—50% better wash fastness (SNV—Test No. 95811/1961) than dyed fabrics obtained by first pad-dyeing with an organic dye liquor and subsequently finishing from an organic finishing bath.

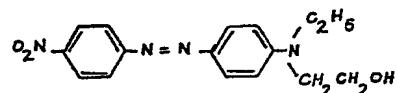
## EXAMPLE 35

Example 34 is repeated but 3 g of the red dyestuff employed in Example 18 are used in lieu of the yellow dyestuff.

Red-dyed fabrics of similar good properties as those of the yellow dyeings of Example 34 are obtained. Those red dyeings are of about 20% better fastness to perspiration (SNV—Test No. 95824/1961) than red dyeings obtained by a two-stage dyeing and finishing treatment.

## EXAMPLE 36

5 g of the dyestuff of the formula



are dissolved in 888 g of a mixture of solvents consisting of 90% by weight of trichloroethylene and 10% by weight of 2-methoxy ethanol. 80 g of a 25% solution of a condensation product from stearic acid, paraformaldehyde and melamine (produced according to Example 1 of German patent application No. 1,044,402 or, without the use of triethanolamine of Example 1 of Swiss Patent No. 374,830) admixed with paraffin (M.P. 52—54°) in a ratio of 1:1 in trichloroethylene, and 20 g of a 50% solution of zirconium isopropylate in isopropanol are added as hardening agent. Cellulose triacetate fabric is impregnated with the clarified, intensively red coloured dye solution and dried as described in Example 1 (bath pick-up about 80%). The impregnated and dried fabric is then thermofixed for 90 seconds in a 220° hot airstream.

A level and well developed scarlet dyeing is obtained which has good fastness to dry cleaning. In addition to good water repellency, the fabric is distinguished by a pleasant, full feel.

By using instead of the 20 g of 50% solution of zirconium isopropylate, 20 g of a 25% solution of maleic acid in isopropanol as hardening agent and following the procedure described in this Example, finished dyeings having similar valuable properties are obtained.

## EXAMPLE 37

3 g of the same red dyestuff as used in Example 18 are dissolved in 877 g of a solvent mixture consisting of 847 g of tetrachloroethylene and 30 g of dimethyl acetamide, 100 g of a 25% solution of a condensation product from stearic acid, paraformaldehyde and melamine (produced according to German patent application No. 1,044,402, Example 1), mixed with paraffin (M.P. 52—54°) in a ratio of 1:1 in trichloroethylene, and 20 g of a 50% solution of zirconium isopropylate in isopropanol are added as hardening agent. Cellulose triacetate fabric is impregnated with the clarified, intensively red coloured dye solution and dried as described in Example 1 (liquor content about 80%). The impregnated and dried fabric is then thermofixed for 90 seconds in a 220° hot airstream. 5

A level and well developed red dyeing is obtained which has good fastness properties and especially good fastness to perspiration. In addition to good water repellency, the fabric is distinguished by a pleasant, full handle. 10

By using instead of the 20 g of 50% solution of zirconium isopropylate, 20 g of a 25% solution of maleic acid in isopropanol and following the procedure described in this Example, finished dyeings having similar valuable properties are obtained. 15

By using in this Example 37 instead of 30 g of dimethyl acetamide, the same amount of one of the water miscible solvents mentioned in the following Table IV column 2 with otherwise the procedure given in this Example, then level and well developed scarlet dyeings on cellulose triacetate fabric are also obtained which have similar good fastness to dry cleaning. The fabric has very good water repellency and a pleasant full feel. 20

TABLE IV

Example No.	water miscible solvents
38	<i>n</i> -propanol
39	isopropanol
40	<i>n</i> -butanol
41	ethylene glycol monomethyl ether
42	tetrahydrofurfuryl alcohol
43	ethylene glycol
44	1,2-propylene glycol
45	dioxan
46	diethyl formamide
47	dimethyl formamide
48	pyridine

By using in Examples 37 to 48, instead of 847g of tetrachloroethylene, the same amount of one of the hydrocarbons or chlorinated hydrocarbons mentioned in the following Table V, column 2, and otherwise following the procedure given in Example 37, level and well developed red dyeings on cellulose triacetate fabric are also obtained.

TABLE V

Example No.	hydrocarbon or chlorinated hydrocarbon
49	toluene
50	xylene
51	trichloroethylene
52	carbon tetrachloride

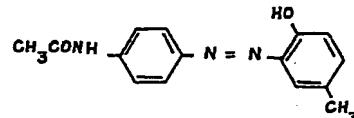
If cellulose-2½-acetate is used in Examples 37 to 52 instead of cellulose triacetate then, with otherwise the same procedure as given, well developed and strongly coloured red dyeings are also obtained on the fibre material mentioned, combined with good water repellency and a pleasant, full feel.

5

5

## EXAMPLE 53

6 g of the dyestuff of the formula



10 are dissolved in 800 g of a mixture of solvents consisting of 99% by weight of trichloroethylene and 1% by weight of dimethyl formamide and a solution of 10 g of a condensation product from melamine, paraformaldehyde, phthalic acid anhydride and octadecyl alcohol (obtained according to Swiss Patent No. 388,901, Example 1), 15 25 g of paraffin (M.P. 52—54°) and 10 g of zirconium isopropylate in about 100 g of trichloroethylene is added. The weight of the liquor is then made up to 1000 g with trichloroethylene. The yellow solution is clarified and cellulose - 2½ - acetate fabric is impregnated therewith as described in Example 31. The dyeing is then thermofixed for 90 seconds in a 190° hot airstream.

10

15 A level and well developed yellow dyeing on the material mentioned is obtained which, at the same time, has a good water repellent effect.

20 When the thermofixing is performed by treatment with high frequency alternating currents, IR irradiation or by contact heat instead of by means of a hot airstream and otherwise the procedure given in the Example is followed, then level and well developed yellow dyeings combined with good water repellency of the material mentioned are also obtained.

15

20

25 Example 53 is repeated but the dyestuff used therein is replaced by 5 g of the yellow dyestuff employed in Example 17, and using 70 g of a solution of 10 g of the same condensation product as described in Example 53, 25 g of paraffin and 10 g of zirconium propylate in 25 g of trichloroethylene, and as solvent mixture 927 g consisting of 897 g of tetrachloroethylene and 30 g of dimethyl formamide.

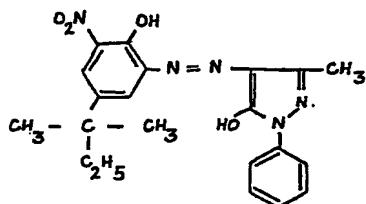
25

30 The resulting yellow cellulose-2½-acetate fabric has a similar good water repellency, and better fastness to crocking and dry-cleaning than fabrics dyed in a two-stage dyeing and finishing treatment.

30

## EXAMPLE 55

10 g of the 1:2 chromium complex of the azo dyestuff of the formula



5 are dissolved in 910 g of a mixture of solvents consisting of 90% by weight of trichloroethylene and 10% by weight of isopropanol. 60 g of a 50% solution of methyl hydrogen polysiloxane (viscosity about 30 cP) at 25° in trichloroethylene, and 20 g of a 50% solution of titanium tetrabutylate in butyl alcohol are added to this solution. Cellulose-2½-acetate is treated as described in Example 31 with the red, clarified dye solution. After drying, the dyeing is thermofixed for 90 seconds in a 200° hot airstream.

10 A strongly coloured, level and well developed red dyeings having good fastness to perspiration is obtained. The fabric has good water repellency and a soft, very smooth handle.

15 By using instead of trichloroethylene, the same amounts of a mixture of trichloroethylene and xylene (weight ratio 1:1) or, using instead of isopropanol the same amount of a mixture of isopropanol and dimethyl formamide (weight ratio 9:1) with otherwise the same procedure as given in the Example, similar results are obtained.

20 By using instead of the dyestuff mentioned in this Example, one of the dyestuffs mentioned in the following Table VI, column 2, with otherwise the procedure given in the Example, stongly coloured, level and well developed cellulose-2½-acetate dyeings in the shades given in column 3 are also obtained. The fabric also has very good water repellency and a soft, silky feel.

TABLE VI

Example No.	dyestuff	shade on cellulose- $2\frac{1}{2}$ -acetate
56	1:2 cobalt complex of the compound 	yellow-brown
57	1:2 chromium complex of the compound 	yellow
58	1:2 chromium complex of the compound 	brownish red

If in Examples 55 to 58 instead of cellulose- $2\frac{1}{2}$ -acetate, cellulose triacetate is used then with otherwise the same procedure as given, well developed and strongly coloured dyeings on the fibre material mentioned are obtained. The material has the same hydrophobic properties as well as the characteristic feel given.

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15

## EXAMPLE 59

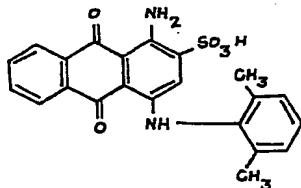
0.1 g of the same yellow dyestuff as used in Example 17 is dissolved in 927 g of a mixture of solvents consisting of 897 g of tetrachloroethylene and 30 g of dimethyl acetamide. 50 g of a 60% solution of methyl hydrogen polysiloxane (viscosity about 30 centipoises at 25°) in tetrachloroethylene, and 20 g of a 50% solution of titanium tetrabutylate in butyl alcohol are added to this solution. Cellulose- $2\frac{1}{2}$ -acetate is treated as described in Example 31 with the yellow, clarified dye solution. After drying, the dyeing is thermofixed for 90 seconds in a 200° hot airstream.

A level and well developed yellow dyeing of light colour depth having good fastness to perspiration and dry-cleaning is obtained. The fabric has good water repellency and a soft, smooth handle.

The resulting fabric has better fastness to dry cleaning and a hydrophobic value (determined by the AATCC Test No. 22—1952) which is about 50% better than that obtained with fabrics dyed and finished correspondingly in a two-stage treatment.

## EXAMPLE 60

2 g of the dyestuff of the formula



5 are dissolved in 942 g of a mixture of solvents consisting of 90% by weight of trichloroethylene and 10% by weight of dioxan which in addition contains 2 g of a condensation product from oleic acid and ethylene oxide (mol ratio about 1:7.5). 50 g of a 10% solution, obtained by precipitating a fluorochemical resin obtained by the methods described in U.S. patent No. 2,803,615, by adding ethanol, drying and dissolving the precipitate in a solvent mixture consisting of butyl acetate and trichloroethylene in a volume ratio of 2:1, are added. Cellulose-2½-acetate fabric is impregnated with this intensively blue coloured clear dye solution and squeezed out to a liquor content of about 80% as described in Example 31 and is then dried. The dried fabric is then thermofixed in a 200° hot airstream for 90 seconds.

10 A strongly coloured, level and well developed blue dyeing on the fibre material mentioned which has good fastness to dry cleaning is obtained. In addition the fabric has excellent oil and good water repellency.

15 By replacing the copolymerize containing fluorine mentioned above by the same amount of an adduct of 2 mols of N-β-hydroxyethyl-N-propyl-perfluoroctane sulphonic acid amide and 1 mol of toluylene di-isocyanate, a dyed and finished fabric having similar properties is obtained.

## EXAMPLE 61

20 1 g of the blue dyestuff mixture employed in Example 19 is dissolved in 950 g of a solvent mixture consisting of 920 g of tetrachloroethylene and 30 g of dimethyl acetamide which in addition contains 2 g of a condensation product from oleic acid and ethylene oxide (mol ratio about 1:7.5). 40 g of a 10% solution, obtained by precipitating a fluorochemical resin obtained by the methods described in U.S. patent No. 2,803,615, by adding ethanol, drying and dissolving the precipitate in a solvent mixture consisting of butyl acetate and trichloroethylene in a volume ratio of 1:2, are added. Cellulose-2½-acetate fabric is impregnated with this intensively blue coloured clear dye solution and squeezed out to a liquor content of about 80% as described in Example 31 and is then dried. The dried fabric is then thermofixed in a 200° hot airstream for 90 seconds.

25 A level and well developed blue dyeing on the fibre material mentioned of good colour depth, which has good fastness to dry cleaning and to perspiration is obtained. 30 The fabric possesses good oil and good water repellency. Water repellency of the fabric is about 45% better than that of the correspondingly dyed and finished fabric produced in a two-stage treatment, the water repellency values being determined by the AATCC Test No. 22—1952.

## EXAMPLE 62

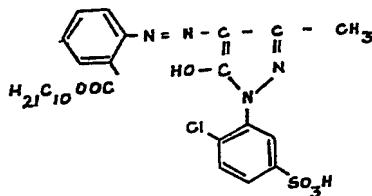
35 Example 61 is repeated, but with 5 g of the yellow dyestuff employed in Example 17, and a yellow fabric of the same good properties as that of Example 61 is obtained. 40 Water repellency according to the AATCC Test No. 22—1952 of the fabric is about 25% better than that of a similar fabric produced by a two-stage treatment.

## EXAMPLE 63

45 Example 61 is repeated, but with 3 g of the red dyestuff employed in Example 18, and a red fabric of the same good properties as that of Example 61 is obtained. 45 Water repellency according to the AATCC Test No. 22—1952 of the fabric is about 100% better than that of a similar fabric produced by a two-stage treatment.

## EXAMPLE 64

10 g of the dyestuff of the formula



5 are dissolved in 970 g of a mixture of solvents consisting of 95% by weight of tetrachloroethylene, 3% by weight of dimethyl acetamide and 2% by weight of the 5  
oleic acid/ethylene oxide condensation product used in Example 1. 20 g of a solution containing 30% of a vinyl chloride-vinyl isobutyl ether copolymerize (weight ratio about 3:1) in a mixture of 1,1,1-trichloroethane/butyl acetate (volume ratio 1:1) are added. Cellulose-2 $\frac{1}{2}$ -acetate is impregnated as described in Example 1 with the 10  
clarified yellow dye solution obtained and then dried. The impregnated and dried fabric is then thermofixed for 120 seconds in a 190° hot airstream.

A strongly coloured, level and well developed yellow dyeing on the material mentioned having good fastness to crocking, washing and perspiration is obtained. The fabric has a voluminous handle. The filling action of the finish can be further increased by the addition of 5 g of polyacrylic acid butyl ester to the impregnation liquor (German patent No. 626,920, Example 1). 15

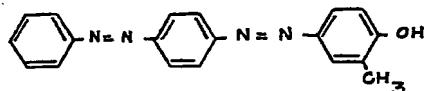
## EXAMPLE 65

20 3 g of the same red dyestuff as employed in Example 18 are dissolved in 942 g of a mixture of solvents consisting of 912 g of tetrachloroethylene, 30 g of dimethyl acetamide, and 5 g of the oleic acid/ethylene oxide condensation product as used in Example 1 and 50 g of a solution containing 30% of a vinyl chloride-vinyl isobutyl ether copolymerize (weight ratio about 3:1) in a mixture of 1,1,1-trichloroethane/butyl acetate (volume ratio 1:1) are added thereto. Cellulose-2 $\frac{1}{2}$ -acetate is impregnated as described in Example 1 with the clarified red dye solution obtained and then dried. 25  
The impregnated and dried fabric is then thermofixed for 120 seconds in a 190° hot airstream.

A level and well developed red dyeing of great colour strength on the material mentioned is obtained, which dyeing has good fastness to dry cleaning, washing and perspiration. The light fastness of the dyed fabric is more than 100% better than that of similar fabric obtained by first dyeing and then finishing separately in a two-stage treatment. The fabric has a voluminous handle. The filling action of the finish can be further increased by the addition of 5 g of polyacrylic acid ester to the impregnation liquor (German patent No. 626,920, Example 1). 30

## EXAMPLE 66

35 Similarly satisfactory reddish yellow dyeings having similar good properties and also a strong, voluminous feel are obtained on repeating the above Example 64, but using 5 g of the dyestuff of the formula 35



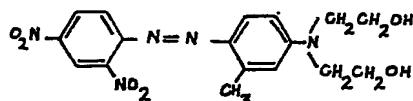
40 instead of 10 g of the dyestuff mentioned in 1000 g of dye liquor.

By repeating Examples 64 to 66, but using instead of dimethyl acetamide, one of the water miscible solvents mentioned in the above Table I column 2 in the amounts given in column 3 of the same Table, also level and well developed dyeings on cellulose-2 $\frac{1}{2}$ -acetate fabric having similar good fastness properties and voluminous handle are obtained.

45 By using in Example 64, instead of 95% by weight of tetrachloroethylene the same amount of one of the hydrocarbons or chlorinated hydrocarbons given in the above Table II, level and well developed yellow dyeings on cellulose-2 $\frac{1}{2}$ -acetate and -triacetate fabric are also obtained. The fabrics have a voluminous handle.

## EXAMPLE 67

10 g of the dyestuff of the formula



5 are dissolved at room temperature in a mixture of solvents consisting of 933 g of tetrachloroethylene, 30 g of dimethyl acetamide and 2 g of the same condensation product as in Example 1. 25 g of a 10% solution of a butadiene/styrene copolymerize in tetrachloroethylene are added. Cellulose-2½-acetate fabric is impregnated with this violet coloured dyestuff solution, the excess dye liquor is squeezed out to 100% of the dry weight of the goods and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 120 seconds in a 190° hot airstream.

10 In this way a level violet dyeing having good fastness to rubbing, perspiration and dry cleaning is obtained. The fabric has a voluminous feel.

15 By replacing the butadiene/styrene copolymerize by 25 g of a 40% solution of a polyterpene resin (described in French patent No. 1,185,745) in perchloroethylene, a fabric having a full pliable handle and otherwise the same properties is obtained.

## EXAMPLE 68

20 3 g of the same red dyestuff as employed in Example 18 are dissolved at room temperature in a mixture of solvents consisting of 915 g of tetrachloroethylene, 30 g of dimethyl acetamide and 2 g of the same condensation product as in Example 1. 25 g of a solution containing 20% paraffin oil and 40% of a polyterpene resin in a solvent mixture of gasoline and tetrachloroethylene are added. Cellulose-2½-acetate fabric is impregnated with this dyestuff solution, the excess dye liquor is squeezed off to have a pick-up of 100% of the dry weight of the goods and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 120 seconds in a 190° hot airstream.

25 In this way a level red dyeing having good fastness to washing, perspiration and dry cleaning is obtained. The fabric has a voluminous handle.

30 Its fastness to washing (SNV—Test No. 95811/1961) and fastness to perspiration (SNV—Test No. 95824/1961) are about 20% better and its light fastness is more than 100% better than these fastnesses in the corresponding dyeings obtained in a two-stage treatment.

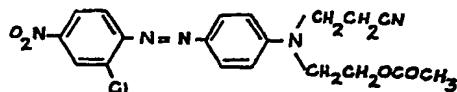
35 By using instead of the dyestuff mentioned in the above Example 68 those given in the following Table VII column 2 with otherwise the procedure described in the Example, then strongly coloured, level dyeings having similar good properties are obtained. The shades thereof are given in the last column of the Table. In each of those cases, the fabric has a voluminous handle.

TABLE VII

Example No.	dyestuff	shade on cellulose- 2 <sub>1</sub> -acetate
69		greenish yellow
70		yellowish orange
71		scarlet
72		blue
73		blue
74		blue

## EXAMPLE 75

5 g of the dyestuff of the formula



5 are dissolved in 935 g of a mixture of solvents consisting of 903 g of tetrachloroethylene and 30 g of dimethyl acetamide and containing 2 g of a stearyl alcohol/ethylene oxide condensation product (mol ratio 1:5), and 50 g of a 50% solution of a dimethyl polysiloxane in tetrachloroethylene are added. 5

10 After filtering the solution, cellulose-2½-acetate is impregnated with the filtrate obtained at room temperature. Excess dye liquor is squeezed out to about 80% of the dry weight of the goods. The impregnated fabric is then dried at 40—50° and thermofixed for 90 seconds in a 200° hot airstream. 10

In this way a strongly coloured, level orange dyeing which is fast to rubbing is obtained. The fabric has a voluminous feel.

15 By replacing in this Example, the 2 g of condensation product of stearyl alcohol and ethylene oxide (mol ratio 1:5) by 15

- a) 2 g of a condensation product of stearyl alcohol and ethylene oxide (mol ratio 1:10),
- b) 4 g of a condensation product of oleyl alcohol and ethylene oxide (mol ratio 1:5),
- c) 2 g of a condensation product of oleyl alcohol and ethylene oxide (mol ratio 1:10),
- d) 3 g of a condensation product of lauryl alcohol and ethylene oxide (mol ratio 1:5),
- e) 2 g of a condensation product of lauryl alcohol and ethylene oxide (mol ratio 1:10),
- f) 3 g of a condensation product of *p*-nonylphenol and ethylene oxide (mol ratio 1:9),
- 25 g) 2 g of a condensation product of oleic acid and ethylene oxide (mol ratio 1:10), or
- 30 h) 4 g of a condensation product of stearic acid and ethylene oxide (mol ratio 1:7),

and otherwise following the procedure given in the Example, orange dyeings having similar good properties are obtained.

## EXAMPLE 76

35 0.2 g of the same yellow dyestuff as used in Example 17 is dissolved in 970 g of a mixture of solvent consisting of 940 g of tetrachloroethylene and 30 g of dimethyl acetamide and containing 2 g of stearyl alcohol/ethylene oxide condensation product (mol ratio 1:5), and 25 g of a 60% solution of a mixture of methyl hydrogen polysiloxane (viscosity at 20° = 25 centipoise) and dimethyl polysiloxane (viscosity at 25° = 750 centistokes) in a weight ratio of 1:1 in tetrachloroethylene are added. 35

40 Cellulose-2½-acetate is impregnated with the solution at room temperature. Excess dye liquor is squeezed off to leave a pick-up of about 80% of the dry weight of the goods. The impregnated fabric is then dried at 40—50° and thermofixed for 90 seconds in a 200° hot airstream. 40

45 In this way a level yellow dyeing is obtained which is fast to crocking and dry cleaning. The fabric has a voluminous handle. 45

## EXAMPLE 77

50 Example 76 is repeated but using 3 of the red dyestuff as employed in Example 18. The resulting fabric is distinguished from the corresponding fabric produced in two stages by a better crocking fastness and an about 50% better light fastness and a softer handle. 50

## EXAMPLE 78

55 Example 76 is repeated, but using 2 g of the blue dyestuff mixture as employed in Example 19. The resulting fabric is distinguished from the corresponding fabric produced in two stages by a better crocking fastness and an about 50% better light fastness and a softer handle. 55

## EXAMPLE 79

5 g of the same yellow dyestuff as used in Example 17 are dissolved in 977 g of a solvent mixture consisting of 943 g of tetrachloroethylene and 30 g of dimethyl acetamide, and 20 g of a solution, in perchloroethylene, containing 10 g of butyl stearate and 4 g of paraffin oil are added thereto.

5

Cellulose-2 $\frac{1}{2}$ -acetate is impregnated with the solution at room temperature. Excess dye liquor is squeezed off to leave a pick-up of about 80% of the dry weight of the goods. The impregnated fabric is then dried at 40—50° and thermofixed for 90 seconds in a 200° hot airstream.

10

10 A level yellow-dyed fabric of great colour depth which is of better crocking and dry cleaning fastness and of a softer handle than a corresponding fabric produced in two separate treatments is obtained.

10

## EXAMPLE 80

15 3 g of the same red dyestuff as used in Example 18 are dissolved in 977 g of a solvent mixture consisting of 943 g of tetrachloroethylene and 30 g of dimethyl acetamide, and 20 g of a solution, in perchloroethylene, containing 10 g of butyl stearate and 4 g of paraffin oil are added thereto.

15

20 Cellulose-2 $\frac{1}{2}$ -acetate is impregnated with the solution at room temperature. Excess dye liquor is squeezed off to leave a pick-up of about 80% of the dry weight of the goods. The impregnated fabric is then dried at 40—50° and thermofixed for 90 seconds in a 200° hot airstream.

20

25 A level red-dyed fabric of great colour depth which is of better crocking and dry cleaning fastness and of a softer handle than a corresponding fabric produced in two separate treatments is obtained.

25

25 2 g of the same blue dyestuff mixture as used in Example 19 are dissolved in 977 g of a solvent mixture consisting of 943 g of tetrachloroethylene and 30 g of dimethyl acetamide, and 20 g of a solution, in perchloroethylene, containing 10 g of butyl stearate and 4 g of paraffin oil are added thereto.

30

30 Cellulose-2 $\frac{1}{2}$ -acetate is impregnated with the solution at room temperature. Excess dye liquor is squeezed off to leave a pick-up of about 80% of the dry weight of the goods. The impregnated fabric is then dried at 40—50° and thermofixed for 90 seconds in a 200° hot airstream.

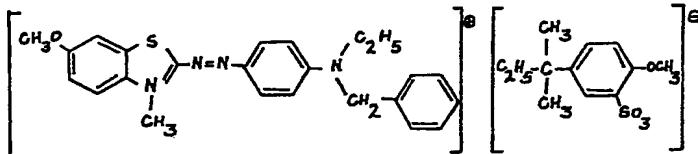
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35 A level blue-dyed fabric of great colour depth which is of better crocking and dry cleaning fastness and of a softer handle than a corresponding fabric produced in two separate treatments is obtained.

35

## EXAMPLE 81

10 g of the dye salt of the formula



40 are dissolved in 950 g of a mixture of solvents consisting of 850 g of trichloroethylene and 100 g of methyl alcohol. 40 g of a trichloroethylene solution which contains 15 g of paraffin oil and 5 g of glycerine trioleate are added. Cellulose-2 $\frac{1}{2}$ -acetate fabric is impregnated with the clear blue dye solution, excess dye liquor is squeezed out to about 80% of the dry weight of the goods and the fabric is dried in a 60—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—220°.

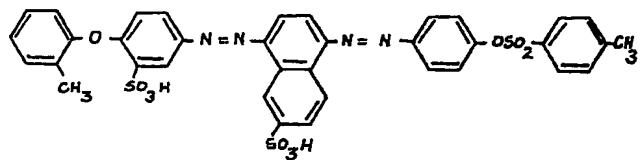
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45 A strongly coloured, level blue dyeing is obtained which has good fastness to dry cleaning and excellent fastness to rubbing. The fabric has a soft and pliable feel. If the 15 g of paraffin oil are replaced by equivalent amounts of stearic acid butyl ester, then a fabric having a particularly pleasant feel is obtained.

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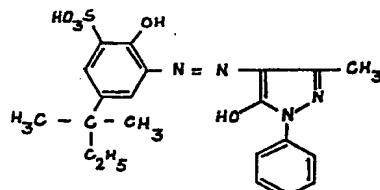
50 By replacing in this Example the 10 g of the dye salt by 0.5 g of the dye salt obtained by precipitation from an aqueous solution of the sodium salt of the dyestuff of the formula

50

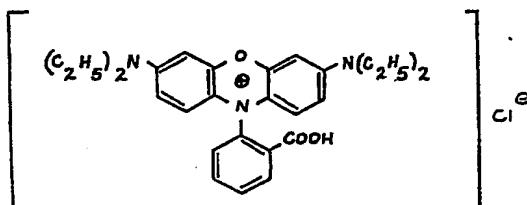


5 with the corresponding amount of dicyclohexylamine, a level orange dyeing, and by replacing the 10 g of the dye salt by 2.0 g of the dye salt, obtained by precipitation from an aqueous solution of the sodium salt of the 1:2 chromium complex of the compound having the formula

5



with the dyestuff of the formula

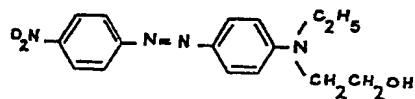


10 level blueish red dyeings are obtained. In both cases the dyeings show the same good properties as mentioned above.

10

EXAMPLE 83

10 g of the dyestuff of the formula



15 are dissolved in about 733 g of a mixture of solvents consisting of 700 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 80 g of a polymerizate of brominated triallyl phosphate containing about 3.6 bromine atoms per monomer unit, in 200 g of benzene is added and the weight of the dye liquor is made up to 1000 g with tetrachloroethylene. Cellulose-2½-acetate fabric is treated as described in

15

20 Example 1 with this liquor. In this way, a strongly coloured, level and well developed red dyeing is obtained. The dyed fabric is, at the same time, excellently flame-proof.

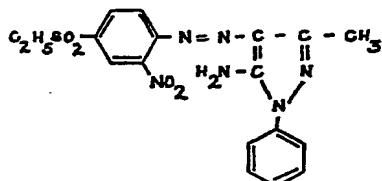
25

These polymerized brominated triallyl phosphates are produced by polymerization of triallyl phosphate in benzene in the presence of benzoyl peroxide until about a third to half of the double bonds have reacted, whereupon the remaining double bonds are brominated by the addition of bromine.

20

## EXAMPLE 84

5 g of the dyestuff of the formula



5 are dissolved in about 733 g of a mixture of solvents consisting of 700 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 80 g of a polymerizate of brominated triallyl phosphate containing about 3.6 bromine atoms per monomer unit, in 200 g of benzene is added and the weight of the dye liquor is made up to 1000 g with tetrachloroethylene. Cellulose-2 $\frac{1}{2}$ -acetate fabric is treated as described in Example 1 with this liquor. In this way, a strongly coloured, level and well developed yellow dyeing is obtained. The dyed fabric is, at the same time, excellent flame-proof.

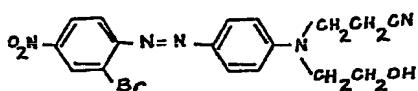
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## EXAMPLE 85

3 g of the dyestuff of the formula



15 are dissolved in about 733 g of a mixture of solvents consisting of 700 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 80 g of a polymerizate of brominated triallyl phosphate containing about 3.6 bromine atoms per monomer unit, in 200 g of benzene is added and the weight of the dye liquor is made up to 1000 g with tetrachloroethylene. Cellulose-2 $\frac{1}{2}$ -acetate fabric is treated as described in Example 1 with this liquor. In this way, a strongly coloured, level and well developed red dyeing is obtained. The dyed fabric is, at the same time, excellently flame-proof.

20

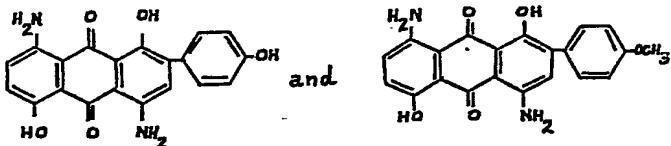
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## EXAMPLE 86

2 g of a mixture of the dyestuffs of the formulae

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in a weight ratio of about 1:1, are dissolved in about 733 g of a mixture of solvents consisting of 700 g of tetrachloroethylene, 30 g of dimethyl acetamide and 3 g of a condensation product of oleic acid and ethylene oxide (mol ratio about 1:7.5). A solution of 80 g of a polymerizate of brominated triallyl phosphate containing about 3.6 bromine atoms per monomer unit, in 200 g of benzene is added and the weight of the dye liquor is made up to 1000 g with tetrachloroethylene. Cellulose-2 $\frac{1}{2}$ -acetate fabric is treated as described in Example 1 with this liquor. In this way, a strongly coloured, level and well developed blue dyeing is obtained. The dyed fabric is, at the same time, excellently flame-proof.

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3 g of the same blue dyestuff mixture as used in Example 19 are dissolved in 962 g of a solvent mixture of 932 g of tetrachloroethylene and 30 g of dimethyl acetamide, 2 g of the oleic acid/ethylene oxide condensation product used in Example 1 and 30 g of a mixture of equal parts of (a) a condensation product of a polyglycidyl ether with hexamethylenediamine as obtained according to Example 1 of Swiss patent application No. 3702/65, published July 14, 1967, wherein the further condensation

5 was interrupted after the viscosity has increased to 30 cP at 25° by the addition of 36 g of acetic acid in 100 ml of water and the solution obtained was brought to a solid content of 80% by distilling off water under reduced pressure, and (b) an organic amine salt of dodecyl benzene sulphonate in a weight to weight ratio of (a):(b) of 1:1 are added thereto. Cellulose-2<sub>1</sub>-acetate fabric is impregnated with the clarified dye solution at room temperature, the goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

10 The resulting blue dyeing is of much better fastness to perspiration than the corresponding fabric padded first with an organic liquor containing the same dyestuff and then finished in a separate organic bath with the same finishing agent.

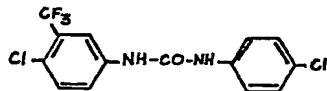
## EXAMPLE 88

15 3 g of the same yellow dyestuff as used in Example 17 are dissolved in 957 g of a solvent mixture consisting of 927 g of tetrachloroethylene and 30 g of dimethyl acetamide. 40 g of a solution containing 33% of a reaction product of 2.5 parts of zirconium *n*-propylate and 1 part of paraformaldehyde in a mixture of *n*-propanol and tetrachloroethylene (volume ratio 1:1) and 5% of zinc octoate, these percentages being calculated on the total weight of the solution, are added. Cellulose-2<sub>1</sub>-acetate fabric is impregnated with the clarified dye solution at room temperature, the goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

20 The resulting yellow dyed fabric has very good anti-slip effect. Its crocking fastness is better than that of a corresponding dyeing obtained by a two-stage treatment.

## EXAMPLE 89

25 3 g of the same yellow dyestuff as used in Example 17 are dissolved in 950 g of a solvent mixture consisting of 920 g of tetrachloroethylene and 30 g of dimethyl acetamide. 2 g of the oleic acid/ethylene oxide condensation product employed in Example 1 and 0.5 g of the bacteriostatic agent of the formula

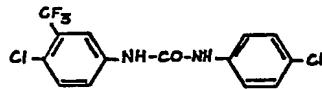


30 dissolved in 50 g of tetrachloroethylene are added thereto. Cellulose-2<sub>1</sub>-acetate fabric is impregnated with the clarified dye solution at room temperature, the goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

35 The resulting yellow-dyed fabric is distinguished by a better bacteriostatic effect than the corresponding fabric dyed and finished in two separate treatments. It is also of much better crocking, dry cleaning and wash fastness.

## EXAMPLE 90

40 3 g of the same red dyestuff as used in Example 18 are dissolved in 950 g of a solvent mixture consisting of 920 g of tetrachloroethylene and 30 g of dimethyl acetamide. 2 g of the oleic acid/ethylene oxide condensation product employed in Example 1 and 0.5 g of the bacteriostatic agent of the formula



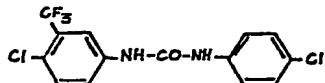
45 dissolved in 50 g of tetrachloroethylene are added thereto. Cellulose-2<sub>1</sub>-acetate fabric is impregnated with the clarified dye solution at room temperature. The goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

50 The resulting red-dyed fabric is distinguished by a better bacteriostatic effect than the corresponding fabric dyed and finished in two separate treatments. It is also of much better crocking, dry cleaning and wash fastness.

## EXAMPLE 91

5 2 g of the same blue dyestuff mixture as used in Example 19 are dissolved in 950 g of a solvent mixture consisting of 920 g of tetrachloroethylene and 30 g of dimethyl acetamide. 2 g of the oleic acid/ethylene oxide condensation product employed in Example 1 and 0.5 g of the bacteriostatic agent of the formula

5



10 dissolved in 50 g of tetrachloroethylene are added thereto. Cellulose-2 $\frac{1}{2}$ -acetate fabric is impregnated with the clarified dye solution at room temperature. The goods are squeezed out to a liquor content of about 100% of their dry weight and the impregnated fabric is dried in a 40—80° hot airstream. The dyeing is then thermofixed for 100 seconds by IR irradiation at 190—210°.

10

The resulting blue-dyed fabric is distinguished by a better bacteriostatic effect than the corresponding fabric dyed and finished in two separate treatments. It is also of much better crocking, dry cleaning and wash fastness.

10

## 15 WHAT WE CLAIM IS:—

1. Process for the dyeing and finishing of cellulose ester fibre material from a single bath, characterised by impregnating or printing this material with a solution containing in combination, organic dyestuff and finishing agent and, optionally, dyeing auxiliaries in a mixture of solvents consisting essentially of

15

20 a) at least 50% by weight of optionally halogenated hydrocarbon boiling between 70 and 150°C, and

20

b) at most 50% by weight of water miscible organic solvent boiling below 210°C, and in the case of the dye solution being applied by impregnating, then removing a large amount of excess treatment liquor from the fibre material, and fixing the dyeing or print by means of thermofixing at temperatures below the softening point of the fibre material.

25

25 2. Process according to claim 1, characterised by the use of a mixture of solvents consisting of 85—99.5% by weight of a halogenated hydrocarbon boiling between 70 and 150°C and 15 to 0.5% by weight of an amide of fatty acid having at most five carbon atoms.

30

30 3. Process according to claim 1 or 2, characterised by the use of a water repellent agent as finishing agent.

30

4. Process according to claim 1 or 2, characterised by the use of an oil-repellent agent as finishing agent.

35

5. Process according to claim 1 or 2, characterised by the use of a finishing agent improving the handle of the fibre material.

35

6. Process according to claim 1 or 2, characterised by the use of a flameproofing agent as finishing agent.

40

7. Process according to claim 1 or 2, characterised by the use of a bacteriostatic agent as finishing agent.

40

8. Process according to claim 1 or 2, characterised by the use of a fungistatic agent as finishing agent.

45

9. Process according to claim 1 or 2, characterised by the use of an antislipping agent as finishing agent.

45

10. Process according to claim 1 or 2, characterised by the use of an antistatic agent as finishing agent.

50

11. Process according to any of claims 1 to 10, characterised by the use of a mixture of different finishing agents.

50

12. Process according to any of claims 1 to 11, characterised by the use of an ether or an ester of polyethylene glycol consisting of a higher aliphatic hydrocarbon radical or the acyl radical of a higher fatty acid with a carbon chain of from 8 to 20 carbon atoms or an alkyl-substituted phenyl radical, the alkyl chain of which having from 6 to 12 carbon atoms and a chain of 4 to 20 ethyleneoxy groups as further auxiliary.

55

13. Process according to any of claims 1 to 12, characterised by the use of polyethylene glycol mono-oleyl ether having from 4 to 10 ethyleneoxy groups as further auxiliary.

55

14. Process according to any of claims 1 to 13, characterised by the use of a

chlorinated aliphatic hydrocarbon having at most two carbon atoms as component a).

15. Process according to any of claims 1 to 14, characterised by the use of tetrachloroethylene or trichloroethylene as component a).

16. Process according to any of claims 1 to 15, characterised by the use of 5 dimethyl acetamide as component b).

17. Process according to any of claims 1 to 16, characterised by the use of metal-free dispersion dyestuffs.

18. Process according to any of claims 1 to 17, characterised by the use of cellulose-2<sub>1</sub>-acetate as fibre material.

10 19. Treatment liquor suitable for the dyeing and finishing of cellulose ester fibre material from a single bath by impregnating or printing and thermofixing the same, characterised in that it consists of a solution containing, in combination, organic dyestuff, finishing agent and, optionally, dyeing auxiliaries, in a mixture of solvents consisting essentially of 10

15 a) at least 50% by weight of optionally halogenated hydrocarbon boiling between 70 to 150°C, and 15

b) at most 50% by weight of water miscible organic solvent boiling below 210°C.

20 20. Cellulose ester fibre material dyed or printed and finished according to a process according to any of claims 1 to 18 or with the treatment liquor according to claim 19. 20

21. A method of dyeing and finishing of cellulose ester fibre material from a single bath substantially as described in Examples 53, 55 to 58, 64, 67, 75, 82 and 83.

22. A method of dyeing and finishing of cellulose ester fibre material from a single bath substantially as described in Examples 1 to 52, 54, 59 to 63, 65, 66, 68 25 to 74, 76 to 81, 82a, 82b and 84 to 91. 25

23. Cellulose ester fibre material dyed and finished from a single bath by a method substantially as described in Examples 53, 55 to 58, 64, 67, 75, 82 and 83.

24. Cellulose ester fibre material dyed and finished from a single bath by a method substantially as described in Examples 1 to 52, 54, 59 to 63, 65, 66, 68 to 30 74, 76 to 81, 82a, 82b and 84 to 91.

25. Treatment liquor as claimed in claim 19 whenever prepared by a process hereinbefore particularly described. 30

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